Adsorption of two antibiotics on biochar prepared in air-containing atmosphere: Influence of biochar porosity and molecular size of antibiotics

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The porous biochar was prepared by pyrolysis of wood at 600–800 °C in the air-containing atmosphere, so as to enhance the biochar’s capacity for adsorption of antibiotics from water. The analytical results obtained from N₂ adsorption/desorption indicated that air addition in pyrolysis atmosphere improved significantly the biochar’s porosity, especially the development of mesopores. The mesoporous biochars showed high adsorption of antibiotics, and the highest adsorption was observed on the A1/5C800 biochar prepared at the air/gas ratio of 1/5 and heat treatment temperature (HTT) of 800 °C. The adsorption isotherm data were well fitted to the Langmuir model, and the maximum adsorptions (Qₘₐₓ) of tetracycline and sulfadiazine on the A1/5C800 sample are 163 and 261 mg/g respectively, which are 18.8 and 52.8 folds of those on the microporous NC800 biochar prepared at the same HTT but in total nitrogen atmosphere. The outstanding performance of mesoporous biochar was linked to the utilization of more inner pore surface for adsorption, which favors the adsorption of smaller-sized sulfadiazine molecules. While the stronger interactions between tetracycline and biochar contributed to the relatively higher adsorption of tetracycline on the microporous biochar. The mesoporous biochar retained most of the adsorption capacity (>50%) in a wide pH range (3.5–10) and with the co-existence of humic acid (10 mg/L). In general, this research provides a simple and green method to enhance the biochar’s efficiency as an adsorbent for remediation of water contaminated by antibiotics.

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1. Introduction

Biochar is an engineered form of black carbon (char) widespread in water, air, soil and sediments. Being the artificial burning or pyrolysis residue of biomass, biochar has attracted much attention of researchers from multiple disciplines because of its promising benefits for carbon sequestration, soil improvement and remediation of contaminated environment [1–3]. Biochar has demonstrated to be a cost-efficient adsorbent for removal of many contaminants such as heavy metals [4–6], dyes [7–9], pesticides [10–12] and antibiotics [13,14] from water, due to the biochar’s rich surface functional groups and porous structure [15]. Furthermore, the diversity on feedstock and optional pyrolysis conditions make it possible to prepare tailor-made biochar products that are specifically efficient for adsorption of target contaminants. For example, the biochar derived from biomass rich in alkali metals has showed high adsorption to cationic heavy metals like Pb²⁺ and Cd²⁺ [16]. Heat treatment temperature (HTT) is also a major factor determining the biochar’s properties. The low HTT is favorable for preparing the biochar rich in polar functional groups (e.g. —OH, —COOH, —CO — and —C≡O), while the high HTT benefits the pore development and often results in the biochar having high surface area [17,18]. Till now, most of laboratory studies on regulating the surface and adsorption properties of biochar focused on feedstock selection and HTT adjustment. And pyrolysis of biomass was commonly carried out in an inert nitrogen atmosphere, or in an oxygen-limited atmosphere in which the exact oxygen content remains unknown. However, the char formation by natural wildfires and artificial burning of biomass is often exposed to air to some extent, and air may be introduced in manufacture of carbon for reducing the energy cost [19,20]. Recently, Xiao et al. [21] have found that the thermal air oxidation at 400 °C could increase biochar’s porosity and adsorptivity of neutral organic molecules, and Zhu et al. [22] reported that the biochar’s porosity could be further enhanced by thermal treatment at 700–800 °C in the mixed air/nitrogen gas. Although the biochar prepared by air-exposed pyrolysis at 300–400 °C has a low surface area and underdeveloped porosity [21], the effect of pyrolysis at higher HTT in air-containing atmosphere on the porosity of biochar remains unclear.

The frequent occurrence of water contamination by antibiotics leads to the increasing concern on their potential adverse impacts on human health and ecosystems [23], and biochar and biomass-derived carbons
have been adopted to remove antibiotics from water because of their cost-efficiency and easy availability [24–27]. The biochar and carbons’ adsorption to organic contaminants is largely dependent on their porosity, namely the pores of biochar/carbons should be large enough to make their inner surface accessible to organic molecules [27–29]. Thermal treatment of biochar in the mixed air/nitrogen atmosphere could dramatically enhance biochar’s porosity and the adsorption of antibiotic tetracycline [22]. However, the performance of biochar prepared by direct pyrolysis in the air-containing atmosphere on adsorption of antibiotics has not been investigated till now.

In this work, the biochar was prepared by pyrolysis of a pinewood in a tube furnace using continuous air/nitrogen flow containing a quantitative amount of air. The change of biochar’s porosity with HTT and air/gas ratio was investigated, and corresponding change of biochar’s adsorption capacity was evaluated using two antibiotics (sulfadiazine and tetracycline) as the adsorbate. The relationship between biochar’s porosity and adsorption of antibiotics was discussed, and influence of initial pH and co-existing humic acid on the adsorption was evaluated as well.

2. Materials and methods

2.1. Biochar preparation

The biochar samples were prepared by pyrolysis of pinewood (Pinus radiata) sawdust in a quartz tube furnace (ø 80 mm x 4 mm and 100 cm in length) filled with air/nitrogen gas at an atmospheric pressure that was maintained via a continuous gas flow. When the air-containing atmosphere was used in pyrolysis, air flow at a rate of 50 or 25 mL/min was switched in and mixed with nitrogen flow at a rate of 200 or 225 mL/min in a mixer that was connected to the tube of furnace. So the air/gas ratio (v/v) used in this study was 1/5 or 1/10 of total gas flow (air + nitrogen), respectively. The nitrogen flow rate of 250 mL/min was used for preparing biochars in a total nitrogen atmosphere. Then the furnace was heated to a set HTT (600, 650, 700, 750 or 800 °C) at a heating rate of 8 °C/min, followed by a holding time of 3.0 h. The solid residue in furnace was taken out from the tube after the furnace was cooled to room temperature, and soaked in pure water for 24 h to remove any soluble matter from the biochar. The biochar products obtained by drying in oven were ground <0.15 mm in particle size, and were denoted as A1/5C600, A1/5C700, A1/5C800, A1/10C800, NC800, etc., respectively. The prefix of A1/5 or A1/10 represents the air/gas ratio of 1/5 or 1/10 used, while N indicates the total nitrogen atmosphere. The suffix number denotes the HTT (e.g. 600, 700 or 800 °C) used for pyrolysis.

2.2. Characteristics and porosity measurement of biochars

Elemental analysis (C, H, O) was performed by using an elemental analyzer (Eurovector EA3000, Italy), and the oxygen content was measured with the oxygen analysis model in the same analyzer. The average C, H and O contents of triplicates were used to calculate the biochar’s H/C and O/C atomic ratios. The ash content of biochars was determined by heating the samples at 800 °C for 4 h. Fourier transform infrared (FTIR) spectra were recorded on a Nexus FT-IR spectrophotometer (Nicole, USA) using a KBr pellet. The X-ray diffraction (XRD) measurements were carried out using a powder X-ray diffractometer (PANanalytical Empyrean, Netherlands).

The biochar’s porosity was evaluated using N 2 adsorption/desorption isotherms that were measured at 77 K in a Tristar II 3020 surface area and porosity analyzer (Micromeritics, USA) after vacuum degassing at 473 K for 6 h [22]. The specific surface area (SA BET) was calculated using the Brunauer–Emmett–Teller (BET) method, the micropore area and volume (SA micro and PV micro ) were measured with the t-plot method, and mesopore (pore diameters of 20–500 Å) surface area and volume (SA meso and PV meso ) was established using the Barrett–Joyner–Halenda (BJH) method [30,31]. The pore size distribution (PSD) of pores with diameter ranged from 17 to 1000 Å was obtained from the adsorption data with the BJH method. Average of duplicates was used for characterizing the SA BET, SA micro, SA meso, PV micro and PV meso of biochar samples.

2.3. Adsorption and desorption experiments

Tetracycline (98.0% purity, Aladdin Inc., China) and sulfadiazine (98.0% purity, Aladdin Inc., China) were used to evaluate the adsorption capability of biochars. Both antibiotics are frequently reported contaminants in water [32]. The adsorption of antibiotic by the biochar was determined by batch equilibration (for 48 h at 25 °C) of 10 mg of biochar in aqueous solution of various initial antibiotic concentrations (C0, mg/L) ranged from 6.0 to 48 mg/L. The volume of antibiotic solution used for adsorption experiments was 20 mL for the A1/5C600 and NC800 biochar, 120 mL for the A1/5C800 biochar and 50 mL for other biochar samples, respectively. The volume of antibiotic solution was varied according to the different adsorption capacity of biochar, so as to obtain 20%–80% uptake of initially added antibiotic from solution. Background solution contained 0.02 mol/L NaCl to maintain constant ionic strength. Humic acid (70% purity, Aladdin Inc., China) of 10 mg/L was dissolved in the background solution for the adsorption experiments investigating the influence of co-existing humic acid. The initial pH (pH0) of solution was adjusted to 5.0, except otherwise specified for adsorption experiments at different pHs, which was adjusted with 0.1 mol/L HCl or NaOH solution. The analysis of tetracycline or sulfadiazine concentration in the equilibrium solution (Ce, mg/L) was conducted in a LC-20A HPLC system (Shimadzu, Japan) equipped with an ultraviolet detector. The mobile phase for determining tetracycline was a mixture solution of 0.01 mol/L oxalic acid/acetonitrile/methyl alcohol = 70/25/5 (v/v/v) with a flow rate of 1.0 mL/min, and the ultraviolet wavelength was set at 360 nm. The mobile phase for determining sulfadiazine was a mixture of water (pH = 4.0 adjusted with acetic acid)/acetonitrile = 80/20 (v/v) and the wavelength was set at 264 nm. The limit of detection is 0.02 mg/L for both antibiotics.

The amount of antibiotic adsorbed on biochar (Qe, mg/g) was calculated from the difference in concentration between the initial (C0, mg/L) and the equilibrium (Ce, mg/L) solutions (Eq. (1)). And triplicates of each desorption point were used in every experiment series. The adsorption data were fitted by the Langmuir (Eq. (2)) model to obtain further quantitative information about the adsorption isotherms.

\[ Qe = \frac{Q_e \cdot C_0}{m} \times \frac{V}{1000} \]  
\[ Qe = \frac{Q_{\text{ads}} \cdot b \cdot C_e}{1 + b \cdot C_e} \]  

where V (mL) is the volume of antibiotic solution; and m (g) is the weight of biochar used. Q e is the maximum adsorption capacity (mg/g) based on the monolayer adsorption model, and b (L/mg) is the Langmuir constant.

Desorption experiments were performed on the three biochars (A1/5C800, A1/5C750 and A1/5C700) having shown higher adsorption capacity to antibiotics. After the adsorption equilibrium with the highest C0 (48 mg/L) reached after 48 h, a half volume of supernatant was removed from the equilibrium solution and replaced with water of pH 5.0 immediately. After shaking at 25 °C for another 48 h, another half volume of supernatant was separated out and replaced with water. The amount of antibiotic still adsorbed on biochar (Qes, mg/g) was calculated by analyzing the antibiotic concentration in solution sampled at each step, and triplicates of each desorption point were used in every experiment series.

3. Results and discussion

3.1. Elemental compositions and surface functional groups of biochars

The biochars of high C content (>89% by weight) were obtained by pyrolysis of pine wood at HTT ≥ 600 °C (Table 1). The total amount of C, H and O measured with elemental analyzer accounted for 96.3%–97.4% by weight of the biochars, indicating that the biochars are dominantly composed of carbon (89.2%–94.4% by weight) and organic residues not fully carbonized. The ash contents, being a common indicator of inorganic minerals, were determined to be 1.53%–2.06% by weight of the biochars (Table 1). The analytical results using the scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS) indicate that there is also a very small amount of Ca in some biochars (Table S1 and Fig. S1 of the Supporting information), so the ash in the biochars should be mainly composed of Ca salts. Despite the variety of pyrolysis atmosphere, the higher HTT results in the biochar of higher C content, lower H and O contents (Table 1). The declined H/C and O/C ratios indicate the enhanced aromaticity and reduced polarity of biochar produced at higher HTT, which is consistent with many previous researches [33–36]. At the same HTT, the biochar prepared in the air-containing atmosphere has slightly higher O content and O/C ratio than that obtained in the total nitrogen atmosphere (e.g. A1/5C700 vs. NC700) (Table 1). The higher O/C ratio indicates the higher polarity of the biochar prepared in the air-containing atmosphere. The higher oxygen content indicates more oxygen-containing functional groups on the biochar surface, which can be proved by infrared (IR) spectra of biochar (Fig. 1). The results indicate the remarkable effect of pyrolysis atmosphere on the pore development of biochar, besides the commonly recognized influence of HTT. Only a small increment of N2 adsorption was observed on the biochar samples produced in total nitrogen atmosphere (NC600–800) when the HTT increased from 600 to 800 °C, according to that shown in the inlet of Fig. 3. In contrast, the more dramatic enhancement of N2 adsorption with increase of HTT was observed on the samples prepared in the air-containing atmosphere (air/gas ratio = 1/5). In addition, the Type I isotherms for the biochar prepared in total nitrogen atmosphere (NC700 or NC800) indicate pore structure dominated by micropores, while the Type IV isotherms for the A1/5C700 and A1/5C800 biochars demonstrate the formation of mesopores in these samples. So, air addition in the pyrolysis atmosphere is beneficial for the mesopore development of biochar prepared at high HTT (≥700 °C). This finding has not been reported previously to the best of our knowledge, and bridges a gap in knowledge about the influence of oxygen in the atmosphere on biochar’s porosity. The results can be used to explain the relatively more developed porosity of biochar produced in the oxygen-limited atmosphere than in the total nitrogen atmosphere [37], and do not contradict the results reported by Xiao et al. [21] about the underdeveloped porosity of biochars prepared by air-exposed pyrolysis at lower HTTs (300 and 400 °C).

The influence of air addition in pyrolysis atmosphere on the porosity of biochars was investigated by comparing the pore size distribution of biochars prepared at different conditions. The N2 adsorption/desorption isotherms were used to investigate the influence of HTT and pyrolysis atmosphere on the pore development of biochars. Fig. 3 shows much high N2 adsorption by the two biochars (A1/5C700 and A1/5C800) at the samples prepared at 700 and 800 °C in the air-containing atmosphere. But there was no apparent difference on N2 adsorption/desorption isotherms, indicating that the biochars contain the similar surface functional groups. In addition, the bands corresponding to —OH, C—OH, C=O, C—H and C=C—C groups were observed on all the biochars prepared at various conditions, indicating that the biochars contain the similar surface functional groups.

### Table 1

Elemental compositions of biochar samples prepared at different pyrolysis conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (wt%)</th>
<th>H (wt%)</th>
<th>O (wt%)</th>
<th>H/C a</th>
<th>O/C a</th>
<th>Yield (%)</th>
<th>Ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC600</td>
<td>89.2 ± 0.7</td>
<td>2.34 ± 0.12</td>
<td>5.17 ± 0.04</td>
<td>0.314</td>
<td>0.0435</td>
<td>22.1 ± 0.3</td>
<td>1.65 ± 0.05</td>
</tr>
<tr>
<td>A1/5C600</td>
<td>89.7 ± 0.1</td>
<td>2.19 ± 0.13</td>
<td>5.54 ± 0.17</td>
<td>0.293</td>
<td>0.0463</td>
<td>18.7 ± 0.9</td>
<td>1.80 ± 0.04</td>
</tr>
<tr>
<td>A1/5C650</td>
<td>90.2 ± 0.3</td>
<td>1.83 ± 0.11</td>
<td>4.30 ± 0.28</td>
<td>0.243</td>
<td>0.0357</td>
<td>17.5 ± 0.6</td>
<td>1.53 ± 0.01</td>
</tr>
<tr>
<td>NC700</td>
<td>92.5 ± 0.3</td>
<td>1.43 ± 0.06</td>
<td>2.70 ± 0.15</td>
<td>0.185</td>
<td>0.0219</td>
<td>21.1 ± 0.8</td>
<td>1.86 ± 0.07</td>
</tr>
<tr>
<td>A1/5C700</td>
<td>92.5 ± 0.3</td>
<td>1.36 ± 0.10</td>
<td>2.79 ± 0.02</td>
<td>0.176</td>
<td>0.0226</td>
<td>18.1 ± 0.2</td>
<td>1.93 ± 0.05</td>
</tr>
<tr>
<td>A1/5C750</td>
<td>91.8 ± 0.4</td>
<td>1.26 ± 0.07</td>
<td>3.34 ± 0.06</td>
<td>0.165</td>
<td>0.0273</td>
<td>16.5 ± 0.3</td>
<td>1.87 ± 0.03</td>
</tr>
<tr>
<td>A1/5C800</td>
<td>92.6 ± 0.4</td>
<td>1.32 ± 0.06</td>
<td>2.73 ± 0.19</td>
<td>0.171</td>
<td>0.0221</td>
<td>15.2 ± 0.5</td>
<td>2.06 ± 0.03</td>
</tr>
<tr>
<td>NC800</td>
<td>94.4 ± 0.6</td>
<td>1.25 ± 0.11</td>
<td>1.29 ± 0.06</td>
<td>0.159</td>
<td>0.0103</td>
<td>20.3 ± 0.6</td>
<td>2.02 ± 0.08</td>
</tr>
<tr>
<td>A1/5C850</td>
<td>94.1 ± 0.2</td>
<td>1.11 ± 0.12</td>
<td>1.44 ± 0.02</td>
<td>0.141</td>
<td>0.0115</td>
<td>16.8 ± 0.6</td>
<td>1.80 ± 0.02</td>
</tr>
<tr>
<td>A1/5C900</td>
<td>93.9 ± 1.1</td>
<td>1.00 ± 0.01</td>
<td>1.74 ± 0.11</td>
<td>0.128</td>
<td>0.0139</td>
<td>11.6 ± 0.3</td>
<td>1.95 ± 0.05</td>
</tr>
</tbody>
</table>

a Molar ratios calculated from the C, H and O contents of various biochars.
biochars prepared at different air/gas ratios (Fig. 4). At the same HTT of 700 °C, the air/gas ratio of 1/5 is favorable for the development of mesopores, and the produced biochar (A1/5C700) has a mesopore volume (PVmeso) of 0.171 cm³/g, with mesopore size mainly ranged from 20 to 70 Å. In contrast, the underdeveloped mesoporosity of the biochar (A1/10C700) prepared with a smaller air/gas ratio (1/10) implies that the corresponding content of oxygen in atmosphere is insufficient for pore development. At the same HTT, the mesopore surface area (SAmeso) increased sharply from 29.6 m²/g of the NC700 biochar to 192 m²/g of the A1/5C700 biochar (Table 2), with the increase of air content in atmosphere. However, the micropore surface area (SAmicro) did not change much with variation of air/gas ratio, according to the SAmicro values of NC700, A1/5C700 and A1/10C700 shown in Table 2. This result confirms the determining role of oxygen for mesopore development, but further increase of air ratio in the atmosphere will lead to excessive burn-off of carbon and poor yield of biochar based on our preliminary studies. At the higher HTT of 800 °C, air addition in pyrolysis atmosphere leads to the differentiation of mesopore development. As that can be seen in Fig. 4(a), the peak value of pore size distribution of the A1/5C800 biochar was transferred to smaller size, in comparison with that of the A1/5C700 biochar. At the meantime, larger pores with size of 100–1000 Å were formed due to the over burning of pore wall. At the lower HTT of 600 °C, air addition in pyrolysis atmosphere did not change the porosity of biochar as much as that observed at the HTT of 700 °C. So, HTT is also a determining factor for the pore development of biochars besides the air/gas ratio in atmosphere.

Fig. 5 shows the change of surface area and pore volume of biochars with HTT. The BET surface area (SABET) of biochar increased with HTT in the air-containing atmosphere, which can also be observed on biochar prepared in nitrogen atmosphere [25,38]. Generally, growth of pores during pyrolysis of biomass involves the release of volatiles and hardening of solid char [39,40]. The higher HTT makes more biomass volatilized and leads to creation of more pores. When a certain amount of air was added in the pyrolysis atmosphere, the gradual development of mesopores (20–500 Å) was observed according to the results shown in Fig. 5(a). The SAmeso was enhanced from 34.3 to 192 m²/g with HTT increase from 600 to 700 °C, while the change of the SAmicro was not so distinct. However, when HTT further increased from 700 to 800 °C, a small drop of SAmeso was observed, accompanying with apparent increase of SAmicro. The same change trend of pore volume can be found in Fig. 5(b), the peak value of PVmeso was obtained at the HTT of 700 °C, while both lower and higher HTT is unfavorable for mesopore development. The proportion of PVmeso is even larger than that of micropore volume (PVmicro) for the biochar prepared at 700 °C, according to the PVmeso/PVmicro shown in Fig. 5(b). Further, the data of mesopore surface area and pore volume calculated from the adsorption branches are equivalent to those calculated from the desorption branches of the isotherms (SAmeso/ads vs. SAmesodes and PVmeso/ads vs. PVmesodes in Fig. 5). In summary, the HTT of 700 °C is most suitable for mesopore development of biochar in the air-containing atmosphere, which is similar to that observed on the post thermal treatment of biochar in the air/nitrogen mixture [22]. We suppose that the reasons should be related to the specific arrangement of graphite-like structures in the biochar obtained at HTT of 700 °C [41], and oxygen in the pyrolysis atmosphere should burn the wall of micropores and enlarge some of them into mesopores. This effect of oxygen/air is similar to that occurred in artificial burning of biomass, and can be used to explain the developed mesoporosity of black carbon obtained by burning of rice straw in open field [42]. Xiao and Pignatello [20] has referred this effect as “reaming” of pores, namely the oxidative removal of pore wall matter and/or tarry deposits generated during the pyrolysis. In this study, the pore reaming occurred synchronously with the pore formation during pyrolysis, and higher HTT of 800 °C is unfavorable for mesopore development due likely to the over burning of pore wall by oxygen [22].

3.3. Adsorption of tetracycline and influence of the biochars’ porosity

The effect of porosity enhancement on adsorption property of biochar was investigated by using tetracycline as the target molecule, and the biochar samples prepared at different HTT in the air-containing
atmosphere were used for comparison. The results shown in Fig. 6(a) indicated the dramatic enhancement on tetracycline adsorption by biochar with the HTT increase from 600 to 800 °C. This change tendency of adsorption property is roughly consistent with the SABET change of the biochar prepared at different HTT (Fig. 5(a)), except for the two samples (A1/5C600 and A1/5C750). Further, the A1/5C800 biochar showed far larger adsorption of tetracycline than other samples obtained at same HTT (A1/10C800 and NC800) (Fig. 6(b)), which is also consistent with their rank of SABET (Table 2). To quantitatively compare the adsorption capacity of various biochars, the maximum adsorption (Qmax) was calculated by fitting the adsorption data with the Langmuir model, and the results are shown in Table 3. As can be seen, the three biochars with developed mesoporosity (A1/5C700, A1/5C750 and A1/5C800) showed high adsorption of tetracycline. The Qmax values of these three mesoporous biochars (~80 mg/g) are larger than that of a microporous activated carbon [43], a pineapple peel biochar [44] and an alkali-treated biochar [45], and are close to a chicken bone biochar [46,47], an iron-modified microalgae biochar [48] and a thermally-treated wood biochar [22]. In particular, the Qmax by the A1/5C800 biochar (163 mg/g) is larger than those by other biochars reported in previous researches (Table S2 in Supporting Information for details). Further, the desorption studies indicate the irreversible adsorption of tetracycline by the A1/5C700, A1/5C750 and A1/5C800 biochars (Fig. 6(a)), suggesting the strong affinity of the biochar’s surface to tetracycline. The high adsorption and its irreversibility are beneficial for the biochar’s performance on removal of antibiotics from water, so as to mitigate the environmental hazards of these contaminants [49–51].

Further, according to the isotherms in Fig. 6 and results in Table 3, the gap between different biochars on tetracycline adsorption is much wider than their difference on SABET. The Qmax by the A1/5C800 biochar is 25.4 folds of that by the A1/5C600 biochar, and 18.8 folds of that by the NC800 biochar, while the largest difference on SABET between these biochar samples is close to 2 folds. For exploring the reasons, the adsorption capacity unit surface area (Qmax/SABET) was calculated and listed in Table 3. We can learn that the utilization efficiency of surface area of three mesoporous biochars (A1/5C800, A1/5C750 and A1/5C700) is much larger than the other biochars (A1/10C800, NC800, A1/5C650 and A1/5C600). Therefore, the biochar’s adsorption of tetracycline is dependent more on their porosity than on the surface area, and only the inner surface of those pores with enough large size can be utilized for adsorption of antibiotic molecules. According to the previous reports [22,37,52,53], the pore diameter should be 1.7 times larger than the molecule’s second-widest dimension, otherwise the target molecules cannot be effectively adsorbed because of size exclusion effect. The molecular size of tetracycline simulated with the Molekel 4.3 for Windows software is 14.8 × 9.00 × 7.47 Å, so the pores with diameter smaller than 15 Å would be inaccessible for tetracycline molecules. The theoretical monolayer adsorption of tetracycline unit surface area is calculated to be 0.553 mg/m², which is close to the maximum adsorption unit surface area (Qmax/SAmeso) for most of the biochars (Table 3). The maximum adsorption unit mesopore volume (Qmax/PVmeso) is also close to the theoretical pore filling capacity unit pore volume (740 mg/cm³) for most of the biochars. The higher adsorption of tetracycline by the A1/5C700 biochar than that by the A1/5C750 biochar (Fig. 6(a)) should be due to the larger SAmeso and PVmeso of the former one (Fig. 5). The exceptional high Qmax/SAmeso and Qmax/PVmeso Values for the A1/5C800 biochar should be related to its high ratio of supermicropores (15–20 Å) according to the pore size distribution (Fig. 4(a)), and the larger pores (100–1000 Å) acting as the aisle facilitated the access of inner pore surface to adsorbate. In general, SAmeso is more suitable for predicting the adsorption capacity of biochars to bulky antibiotic molecules than SABET, and the contribution of supermicropores and macropores should also be considered for evaluating the biochars’ adsorption capacity.

### Table 2

<table>
<thead>
<tr>
<th>Biochar</th>
<th>SA_BET (m²/g)</th>
<th>SA_meso (m²/g)</th>
<th>SA_micr (m²/g)</th>
<th>PV_meso (cm³/g)</th>
<th>PV_micr (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1/5C800</td>
<td>738 ± 30</td>
<td>514 ± 17</td>
<td>124 ± 4</td>
<td>0.244 ± 0.011</td>
<td>0.109 ± 0.004</td>
</tr>
<tr>
<td>A1/5C600</td>
<td>483 ± 0</td>
<td>399 ± 6</td>
<td>50.2 ± 7.4</td>
<td>0.199 ± 0.004</td>
<td>0.057 ± 0.013</td>
</tr>
<tr>
<td>NC800</td>
<td>431 ± 18</td>
<td>357 ± 12</td>
<td>40.9 ± 1.8</td>
<td>0.167 ± 0.006</td>
<td>0.031 ± 0.001</td>
</tr>
<tr>
<td>A1/5C700</td>
<td>541 ± 13</td>
<td>358 ± 2</td>
<td>192 ± 1</td>
<td>0.156 ± 0.003</td>
<td>0.171 ± 0.011</td>
</tr>
<tr>
<td>A1/5C750</td>
<td>454 ± 11</td>
<td>339 ± 10</td>
<td>79.8 ± 1.7</td>
<td>0.163 ± 0.007</td>
<td>0.072 ± 0.001</td>
</tr>
<tr>
<td>NC700</td>
<td>369 ± 4</td>
<td>310 ± 12</td>
<td>25.6 ± 4.3</td>
<td>0.156 ± 0.007</td>
<td>0.023 ± 0.004</td>
</tr>
<tr>
<td>A1/5C500</td>
<td>391 ± 0</td>
<td>317 ± 4</td>
<td>34.3 ± 4.5</td>
<td>0.159 ± 0.002</td>
<td>0.026 ± 0.006</td>
</tr>
<tr>
<td>NC600</td>
<td>337 ± 25</td>
<td>271 ± 21</td>
<td>29.9 ± 3.3</td>
<td>0.136 ± 0.010</td>
<td>0.025 ± 0.001</td>
</tr>
</tbody>
</table>

### 3.4. Adsorption of sulfadiazine and influence of molecular size

Fig. 7 shows the adsorption of another antibiotic sulfadiazine by the biochars prepared in the air-containing atmosphere, and the NC800 biochar prepared in total nitrogen atmosphere was also included for comparison. The biochars can be ranked according to their adsorption to sulfadiazine in the following order: A1/5C800 > A1/5C750 ≈ A1/5C700 > A1/5C650 > NC800. This rank is similar to the tetracycline adsorption by various biochars (Fig. 6), namely the mesoporous biochars (A1/5C800, A1/5C750 and A1/5C700) showed much higher sulfadiazine adsorption than the other biochars. The desorption studies indicate the irreversible adsorption of sulfadiazine by these mesoporous biochars.
(Fig. 7), which is beneficial for preventing re-release of adsorbed contaminant from the biochars. The $Q_m$ of sulfadiazine by the $A_{1/5}$C800 biochar is 52.8 folds of that by the NC800 biochar (Table 4). As there have been few reports in the literature about the adsorption of sulfadiazine by biochars, the comparison was made by referring to sulfamethazine, another sulfonamide antibiotic that has similar molecular structure and molecular weight to sulfadiazine. The adsorption capacity of sulfadiazine by the three mesoporous biochars ($A_{1/5}$C800, $A_{1/5}$C750 and $A_{1/5}$C700) is much larger than the adsorption of sulfamethazine by tea waste biochars [54], steam-activated plant-derived biochars [55] and $H_3PO_4$-activated bamboo-derived biochars [56]. In comparison with chemical activation methods, addition of air in pyrolysis atmosphere is a more facile and environment-friendly operation to improve the adsorption capacity of biochars. The results also imply that the surface and adsorption properties of chars obtained by natural wildfires and artificial burning will be different from those biochars prepared in inert atmosphere, and partial exposure of air during formation of chars would enhance their performance on adsorption of organic contaminants.

Furthermore, the biochar’s capacity of antibiotic adsorption is related to the molecular size of adsorbate. The molecular size of sulfadiazine simulated with the Molekel 4.3 for Windows software is $14.9 \times 6.31 \times 4.86$ Å, which is smaller than tetracycline. Therefore, the pores with diameter larger than 10 Å could be available for adsorption of sulfadiazine, and the $Q_m/SA_{BET}$, $Q_m/SA_{meso}$ and $Q_m/PV_{meso}$ values of sulfadiazine by the mesoporous biochars ($A_{1/5}$C800, $A_{1/5}$C750 and $A_{1/5}$C700) are all larger than those of tetracycline. However, for the three microporous biochars with underdeveloped mesoporosity ($A_{1/5}$C600, $A_{1/10}$C800 and NC800), the $Q_m/SA_{BET}$, $Q_m/SA_{meso}$ and $Q_m/PV_{meso}$ values of sulfadiazine are all smaller than those of tetracycline. The reasons for such distinction should be related to the different adsorption mechanisms of antibiotics on these two series of biochars. The inner pore surface adsorption dominated the adsorption of antibiotics by the mesoporous biochars, and the smaller-sized sulfadiazine molecules are advantageous over tetracycline molecules for utilization the inner pore surface of biochar. In particular, the $A_{1/5}$C800 biochar has a $Q_m/SA_{BET}$ value close to the theoretical monolayer adsorption of sulfadiazine (0.439 mg/m²), indicating the full utilization of inner pore surface of this biochar. In contrast, most of the inner pore surface of the microporous biochars is not available for adsorption of antibiotics due to the size exclusion effect, and the interactions between biochar and antibiotic molecules would determine the adsorption on the external surface. The tetracycline molecules possess higher aromaticity and more hydroxyl functional groups than the sulfadiazine molecules, so that the interactions such as $\pi-\pi$ electron donor acceptor ($\pi-\pi$ EDA) interaction and H-bonding between biochar and tetracycline molecules [11,57] are stronger, and more tetracycline can be adsorbed on the microporous biochars. Such interactions between tetracycline and the biochars are validated by the FTIR analysis of the biochar after adsorption of tetracycline. The band at 3434 cm$^{-1}$ belonging to hydroxyl groups was
3.5. Influence of pH and co-existing humic acid on adsorption of antibiotics

The A1/5C700 biochar having most developed mesopores was used for investigations about the influence of pH and co-existing humic acid on adsorption of antibiotics. Generally, the gradually reduced sulfadiazine adsorption was observed with the pH increase from 3.5 to 10.0, which should be attributed partly to the electrostatic attraction between the cationic antibiotics and the negatively charged biochar surface. The relatively higher adsorption at the pH 5.0 was resulted from the stabilization of the zwitterions through H-bond formation and π-π EDA interaction [57,58]. The pH increase to an alkalescent level (8.0 or 10.0) would make sulfadiazine molecules exist mainly in anionic form, and the repulsion by the negatively charged biochar surface would lead to the reduced adsorption [25,58]. However, the sulfadiazine adsorption by the A1/5C700 biochar at pH 8.0 and 10.0 could still remain a high level (~70% and ~50% of the Qm at pH 5.0), proving again the determining role of the biochar’s porosity on adsorption of antibiotics. Such high adsorption capacity makes the mesoporous biochar applicable for efficient removal of antibiotics in aqueous system of a wide pH range (3.5–10.0), and also for retention of antibiotics in both acid and basic soils so as to reduce the toxicity and availability of antibiotics to soil organisms [59,60]. The tetracycline adsorption by the A1/5C700 biochar at different pHs ranged from 3.5 to 10.0 was also investigated in the preliminary experiments. However, during the experiments in alkalescent solution of tetracycline (8.0 or 10.0), the visible color change of solution and by-product peaks in the chromatogram of solution samples indicated the readily hydrolysis of tetracycline. Such hydrolysis makes it difficult to determine the true influence of pH on tetracycline adsorption by biochar.

Humic acid is an important dissolved organic matter (DOM) ubiquitous in natural water. The adsorptions of both tetracycline and sulfadiazine by the A1/5C700 biochar with co-introduction of humic acid (10 mg/L) in the antibiotic solution were shown in Fig. 9, and the

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Qm (mg/g)</th>
<th>b</th>
<th>R²</th>
<th>Qo-SA_{\text{SABET}} (mg/m²)</th>
<th>Qo-SA_{\text{meso}} (mg/m²)</th>
<th>Qo-PV_{\text{meso}} (mg/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1/5C600</td>
<td>6.42</td>
<td>0.34</td>
<td>0.946</td>
<td>0.0164</td>
<td>0.187</td>
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<td>NC600b</td>
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<td>0.856</td>
<td>0.0543</td>
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<td>0.959</td>
<td>0.186</td>
<td>0.525</td>
<td>589</td>
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<td>A1/5C700b</td>
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<td>0.121</td>
<td>0.979</td>
<td>0.0385</td>
<td>0.219</td>
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<td>NC700b</td>
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<td>0.987</td>
<td>0.0200</td>
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<td>321</td>
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<td>A1/5C750</td>
<td>88.7</td>
<td>0.196</td>
<td>0.928</td>
<td>0.139</td>
<td>0.629</td>
<td>693</td>
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<td>A1/5C800</td>
<td>163</td>
<td>0.510</td>
<td>0.990</td>
<td>0.220</td>
<td>1.31</td>
<td>1492</td>
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<td>A1/5C800b</td>
<td>26.6</td>
<td>0.558</td>
<td>0.948</td>
<td>0.0551</td>
<td>0.530</td>
<td>467</td>
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<tr>
<td>NC800</td>
<td>8.66</td>
<td>0.218</td>
<td>0.976</td>
<td>0.0201</td>
<td>0.212</td>
<td>279</td>
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### Table 4

<table>
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<tr>
<th>Sample</th>
<th>Qm (mg/g)</th>
<th>b</th>
<th>R²</th>
<th>Qo-SA_{\text{SABET}} (mg/m²)</th>
<th>Qo-SA_{\text{meso}} (mg/m²)</th>
<th>Qo-PV_{\text{meso}} (mg/cm³)</th>
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<tr>
<td>A1/5C600b</td>
<td>2.20</td>
<td>0.273</td>
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<tr>
<td>NC600b</td>
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<td>0.970</td>
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<td>A1/5C650</td>
<td>23.1</td>
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<td>0.913</td>
<td>0.0508</td>
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<td>A1/5C700</td>
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<td>0.981</td>
<td>0.228</td>
<td>0.648</td>
<td>721</td>
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<tr>
<td>A1/10C700b</td>
<td>9.32</td>
<td>0.337</td>
<td>0.990</td>
<td>0.0205</td>
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<td>129</td>
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<tr>
<td>NC700b</td>
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<td>0.905</td>
<td>0.0077</td>
<td>0.096</td>
<td>123</td>
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<tr>
<td>A1/5C750</td>
<td>108</td>
<td>0.820</td>
<td>0.854</td>
<td>0.169</td>
<td>0.765</td>
<td>842</td>
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<tr>
<td>A1/5C800</td>
<td>261</td>
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<td>0.958</td>
<td>0.354</td>
<td>2.11</td>
<td>2395</td>
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<tr>
<td>A1/10C800b</td>
<td>11.4</td>
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<td>0.0236</td>
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<td>NC800</td>
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<td>0.903</td>
<td>0.0115</td>
<td>0.121</td>
<td>159</td>
</tr>
</tbody>
</table>

* Fitting results of tetracycline adsorption data with the Langmuir model.

b The adsorption isotherms of tetracycline by the biochars were shown in Fig. S4 of the Supporting information.

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b The adsorption isotherms of sulfadiazine by the biochars were shown in Fig. S4 of the Supporting information.
developed mesoporosity ($A_{1/5C700}$, $A_{1/5C750}$ and $A_{1/5C800}$) showed high adsorption of tetracycline, and the highest $Q_m$ (163 mg/g) is larger than those by other biochars reported previously. The adsorption of smaller-sized sulfadiazine was further enhanced due to the better utilization of inner pore surface of these biochars. The desorption studies indicate the irreversible adsorption of antibiotics by these mesoporous biochars. In addition, these biochars retained the high adsorption capacity in a wide pH range (3.5–10.0) and with the co-existence of humic acid.

4. Conclusions

In summary, addition of a proper ratio of air in pyrolysis atmosphere can dramatically enhance the porosity of biochars prepared at the relatively high HT (600–800 °C), and in turn increase their adsorption to antibiotics. The results indicate that the HT of 700 °C is most suitable for the biochar’s mesopore development, and the $SA_{meso}$ was enlarged to 192 m$^2$/g with the increase of air/gas ratio to 1/5. The biochars with correspondingly calculated $Q_m$ values were also listed. In comparison with the results without co-existence of humic acid, the remarkably reduced adsorption of both antibiotics (<50%) by the biochar was observed with the co-existence of humic acid. The dropped adsorption should be related to the co-adsorption of humic acid by biochar. Kasozi et al. [61] have investigated the sorption of humic acid on the biochars produced at different temperatures. They found that greater sorption occurred on the biochar made at higher temperature, which is ascribed to more nanopores in this biochar. Pignatello et al. [62] have observed that humic acid acted as the pore blocking agent or competitive adsorbate for wood char, so that the adsorption of organic molecules was suppressed. Qiu et al. [42] have reported that the adsorption of pesticides by biochar was reduced by the co-existence of model DOM because of the blockage of pores by DOM. The results in this study are consistent with these previous researches, and the co-adsorption of humic acid to the biochar reduced the sites available for antibiotic molecules. Despite this fact, there have been some reports about the increased adsorption of antibiotics on biochar with the co-introduction of humic acid [63]. The reasons should be related to the different surface properties of biochars used in different researches. For the biochars with underdeveloped porosity, their adsorption to antibiotics is often limited to a magnitude of <10 mg/g and mainly occurred on the external surface. The surface adhesion of humic acid to these biochars may strengthen their interactions such as H-bonding with antibiotic molecules. However, the mesoporous biochar produced in this study can still adsorb a great amount of antibiotics (>50 mg/g) even with the co-existence of humic acid, and will show high efficiency from removal of antibiotics from wastewater.

Declarations of interest

None.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2018.10.142.

References
